北京理工大學 BEIJING INSTITUTE OF TECHNOLOGY

团结 勤奋 求实 创新

Review of Recycling Technologies for Spent Lithium-ion Batteries

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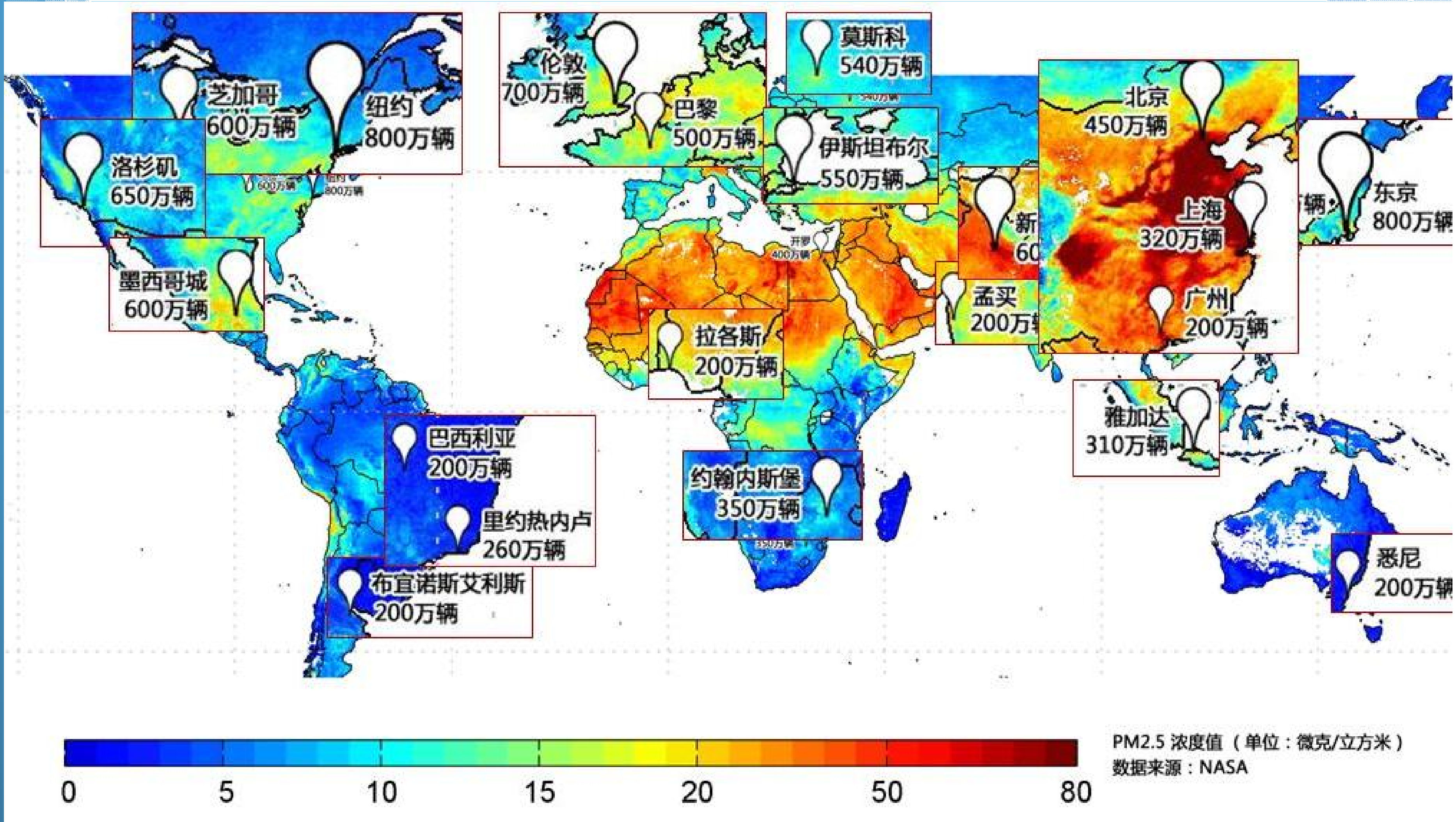
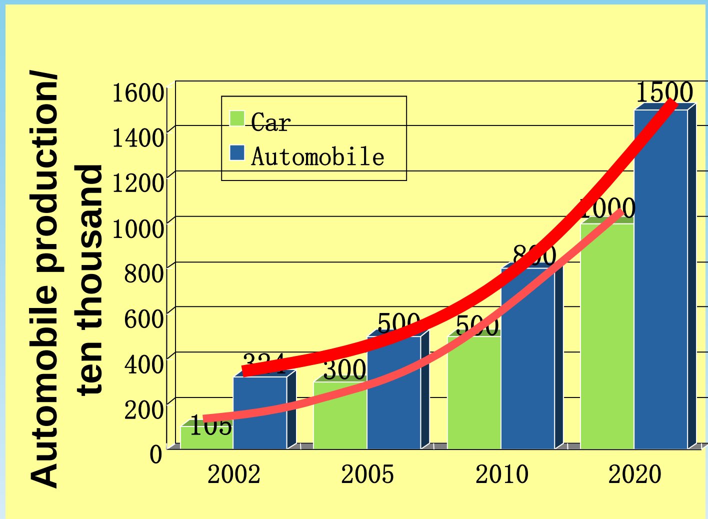
Outline

1. **Current recycling status of spent batteries**
2. **Recycling technologies for spent LIBs**
3. **Typical battery recycling companies in China**



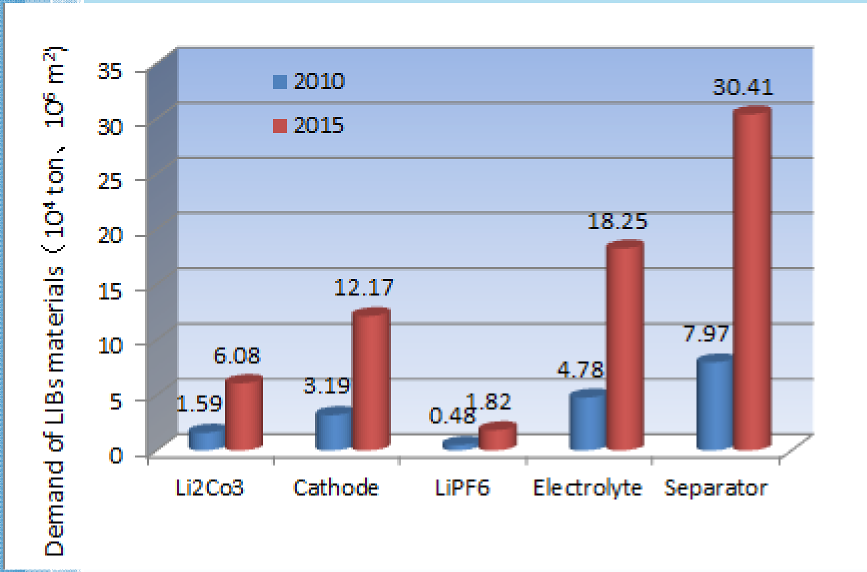
PM2.5 concentration maps of the cities which own more than two million vehicles

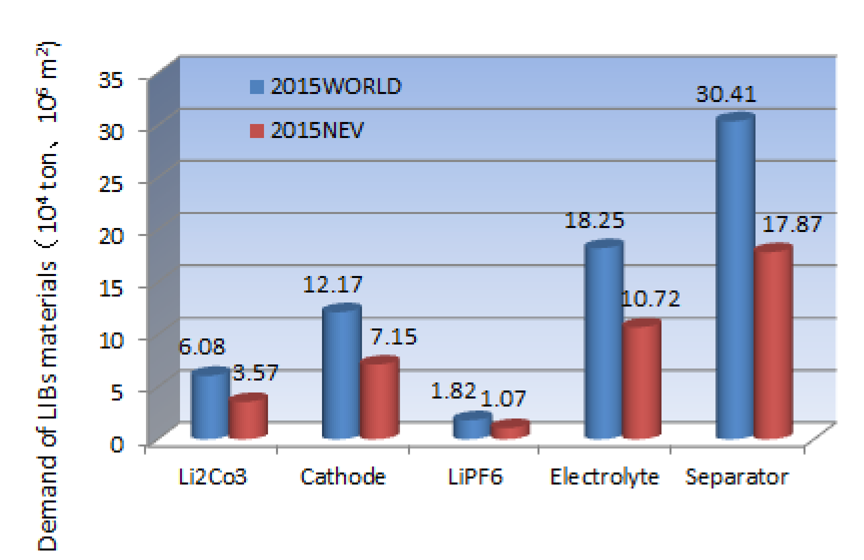
Increasing of roadway traffics bring high pressures to energy and environment



Recycling potential

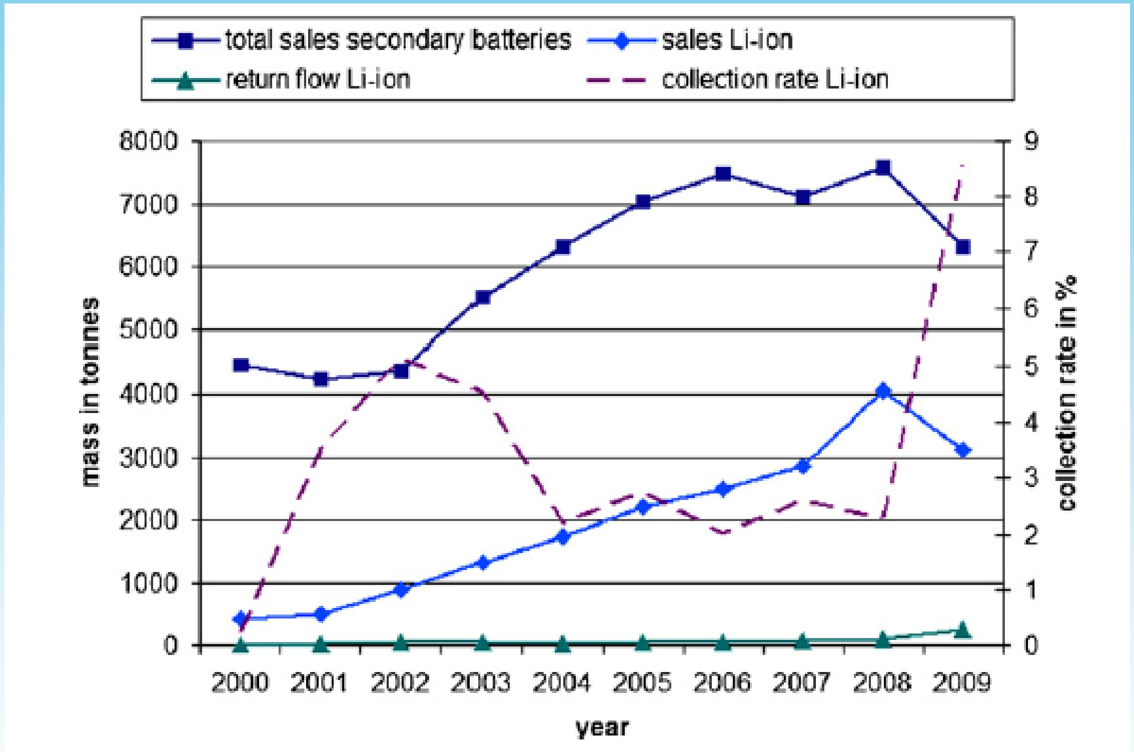
- In 2006 the United States and Europe had the highest proportion, 28.4% respectively 27.2%, of the worldwide Li-ion battery consumption.
- However, their proportion of the worldwide Li-ion battery production was only 0.4% and 2.0%, respectively.
- More than 90% of Li-ion battery cells were produced in Japan, South Korea and China





Demands of battery materials in 2010 and 2015 (left)
Demands forecast of LIBs materials for new energy vehicles in 2015 (right)

Sales, return flows and collection rates of LIBs in Germany (2000-2009)



In spite of the currently low collection rates forecasts show that sales figures will continue to increase up to more than 30,000 tons in 2015 and the market share of Li-ion batteries will be far above 50%. As a consequence also a strong increase of the return flow can be expected. That means that suitable recycling processes have to be established, which have the capacities to process the upcoming recycling flow.

Average material content of potable Li-ion batteries

- **Since all battery producers sell their own specific types of LIBs, it is difficult to specify exact numbers for the material content of a Li-ion battery scrap mixture.**
- **LIBs from a typical production scrap charge have been disassembled by hand and the battery components were separated and weighed.**

Battery component	Product data sheets in mass-%	Self-determined
Casing	~20–25	~25
Cathode material ($LiCoO_2$)	~25–30	~25
Anode material (graphite)	~14–19	~17
Electrolyte	~10–15	~10
Copper electrode foil	~5–9	~8
Aluminium electrode foil	~5–7	~5
Separator	–	~4
Others	Balance	Balance

Safe disposal may become a serious problem

Heavy metals

Hazards

Organic solvents

Air pollution

Fig. 7. Metal alloy (left), slag (middle) and flue dust (right) produced in technical-scale test.

Fig. 3. Metal containing material fractions after crushing and material separation (from left to right: iron-nickel fraction, aluminium fraction, electrode foil fraction).

Challenge and Opportunities of Power Battery

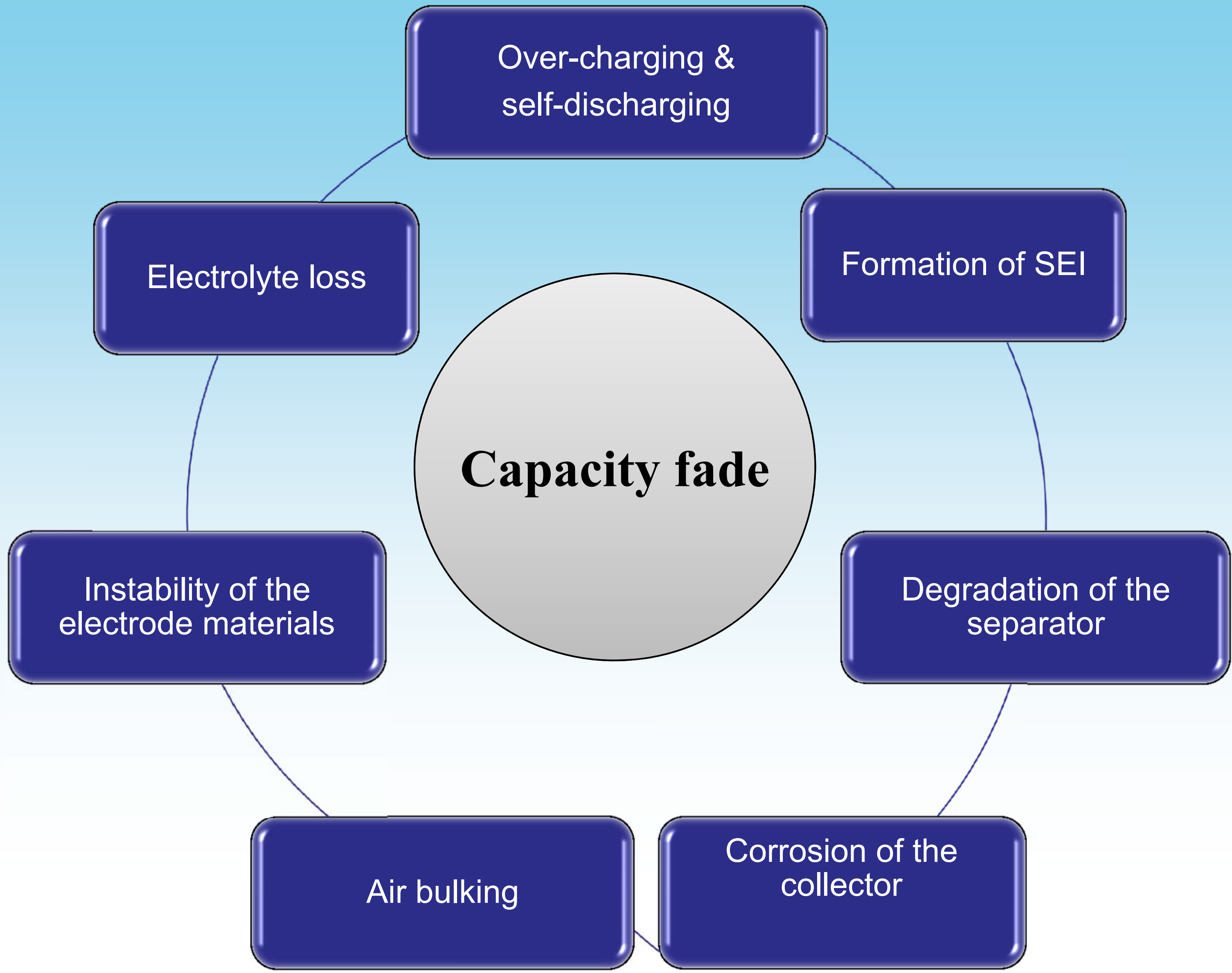
1.Power Density and Energy Density

2. Cost reduction and Safety Issues

3. Battery Recycling Technology

- From the viewpoints of environmental preservation, recovery of major components or valuable resources, and provision of raw materials, the battery recycling is highly desirable in either the present time or the future.

Capacity fade mechanism of Li-ion battery



Recycle Technologies of Spent Lithium ion Batteries

Direct synthesis of electrode materials

- Sol-gel method
- Hydrothermal method
- Co-precipitation method
- Electrochemical method

Chemical treatment

- Acid leaching
- Bioleaching
- Chemical precipitation
- Solvent extraction
- Electrochemical process

Physical treatment

- Thermal treatment
- Mechanical separation
- Mechanochemical process
- Dissolution process

- Reduce scrap volume
- Separate components
- Enrich valuable metals
- Eliminate or reduce danger

(1) Physical Processes –Pretreatment

Mechanical separation

- Mechanical separation techniques intend to separate materials according to different properties like density, conductivity, magnetic behavior, etc.

Thermal processes

- Thermal processes are usually associated with the production of steel, ferromanganese alloys or other metallic alloys.

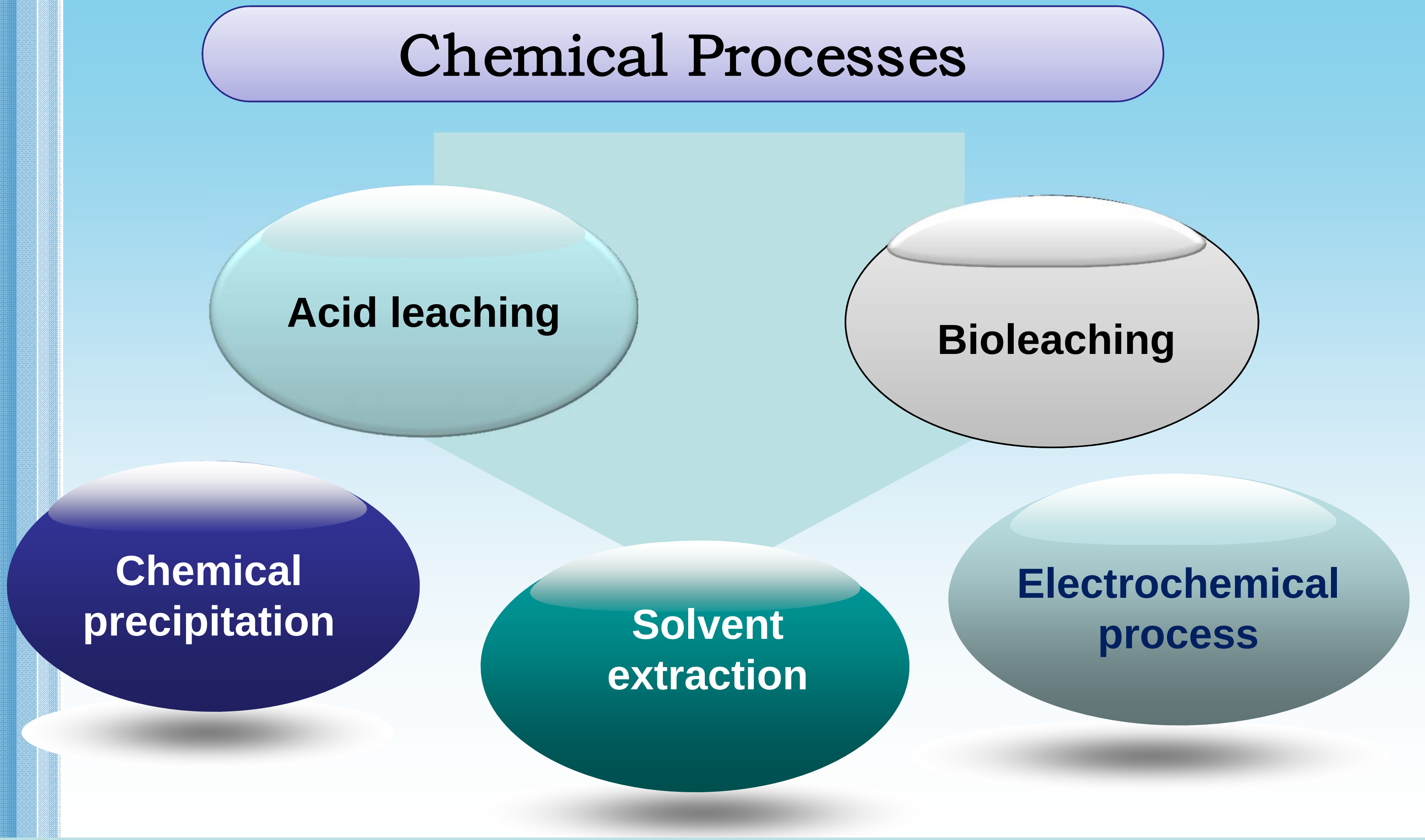
Mechanochemical process

- Mechanochemical process is to use a grinding technique that makes the crystal structure of the positive electrode in the LIB, into disordered system, enabling useful substances such as Co and Li easily extracted by acid leaching at room temperature from the LIBs scraps wastes.

Dissolution process

- Dissolution process is to use special organic reagents to dissolve the adhesive substance (PVDF), which adheres the anode and cathode electrodes, and therefore this process can make powders get separated from their support substrate easily and recovered effectively.

(2)Chemical Processes



Chemical processes are connected to leaching steps in acid or alkaline medium and purification processes in order to dissolve the metallic fraction and recover metal solutions.

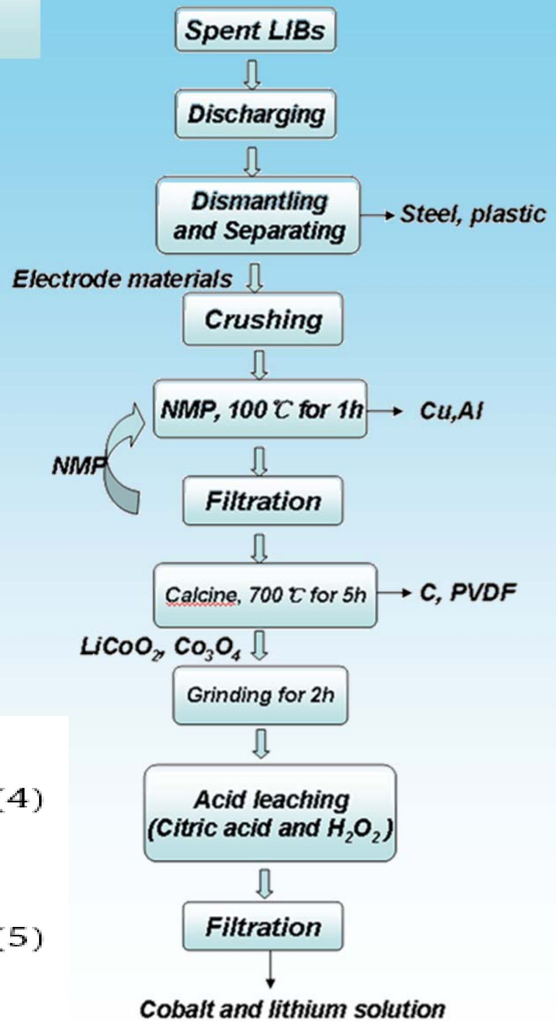
（1）Leaching process for $LiCoO_2$ materials using citric acids as leachant

Spent LIBs from (a) cellular phones and (b) the cathode and anode from a spent LIB

$$6H_3Cit(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 6H_2Cit^-(aq) + 2Co^{2+}(aq) + 4H_2O + O_2(g) \quad (4)$$

$$6H_2Cit^-(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 2Co^{2+}(aq) + 6HCit^{2-}(aq) + 4H_2O + O_2(g) \quad (5)$$

$$6HCit^{2-}(aq) + 2LiCoO_2(s) + H_2O_2(aq) = 2Li^+(aq) + 2Co^{2+}(aq) + 6Cit^{3-}(aq) + 4H_2O + O_2(g) \quad (6)$$



Flowsheet of the hydrometallurgical recycling process for lithium ion secondary rechargeable batteries.

（1）Leaching process for $LiCoO_2$ materials using citric acids as leachant

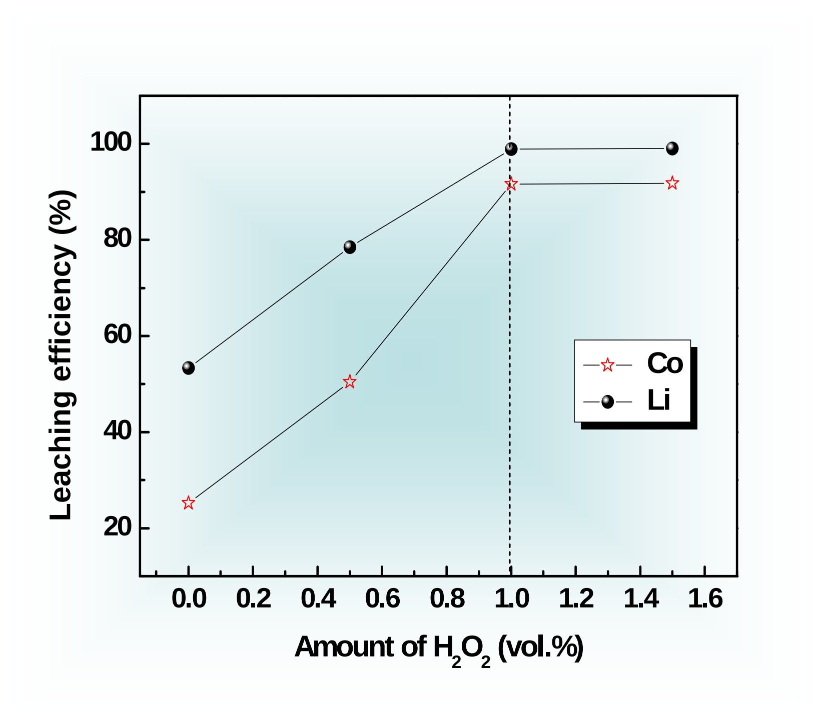


Fig. 9. Effect of H_2O_2 amount on the leaching of waste $LiCoO_2$ with 1.25 M citric acid at 90 °C for 30 min (S:L=20 gL−1 and agitation speed=300 rpm).

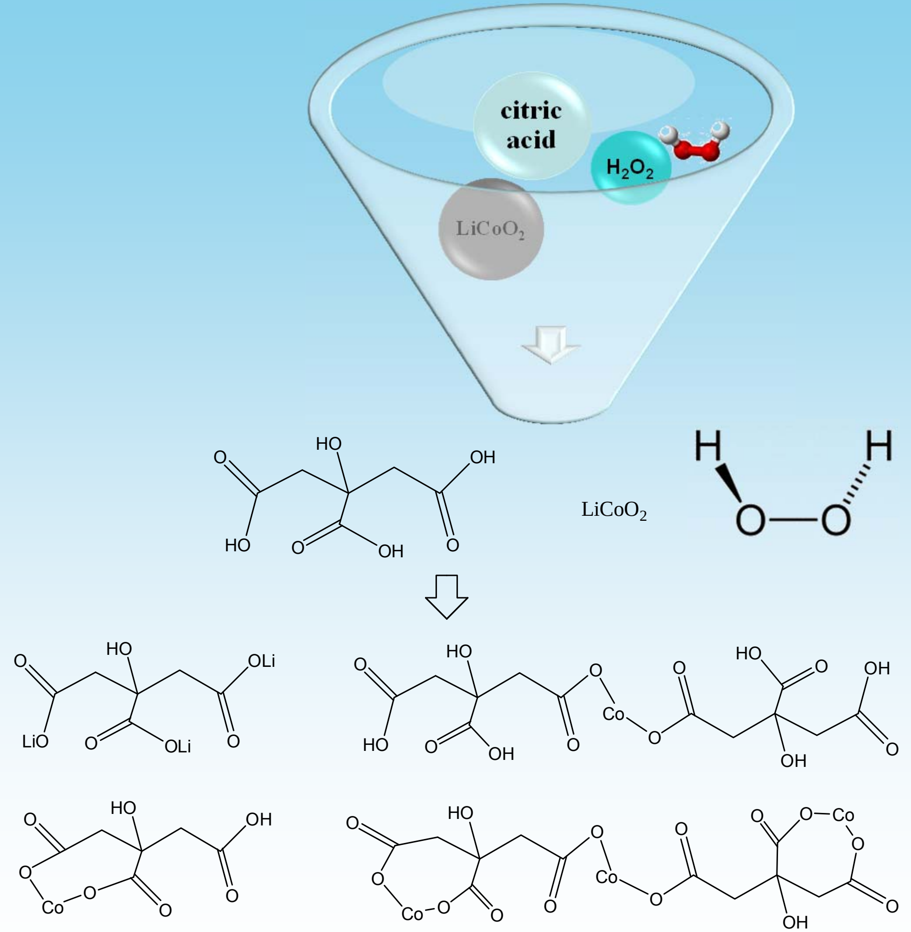


Fig.10 Possible reaction products for citric acid and $LiCoO_2$.

LiLi, WuFeng et al, Journal of Hazardous Materials. 176 (2010), 288-293

（2）Leaching process for $LiCoO_2$ materials using malic acids as leachant

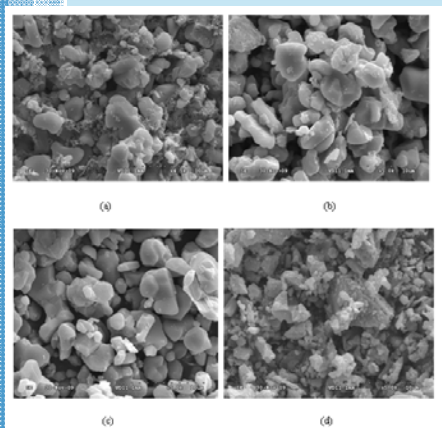


Fig. 1. SEM images of different cathode materials: (a) the dismantled cathodic material from a spent LIB, (b) the cathodic material after treatment with NMP, (c) the cathodic material after dismantling and calcination at 700 °C for 5 h and (d) the leach residues.

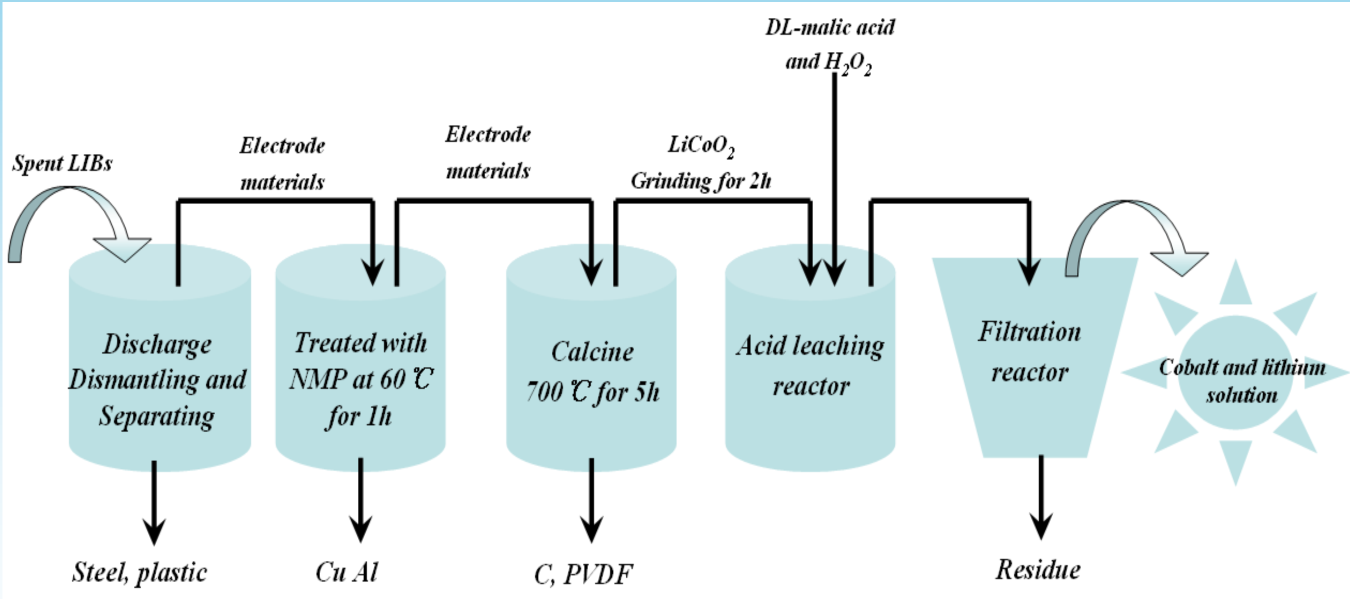


Fig. 2. Flow sheet for the recovery of Co and Li from spent Li-ion batteries using DL-malic acid as a leachant

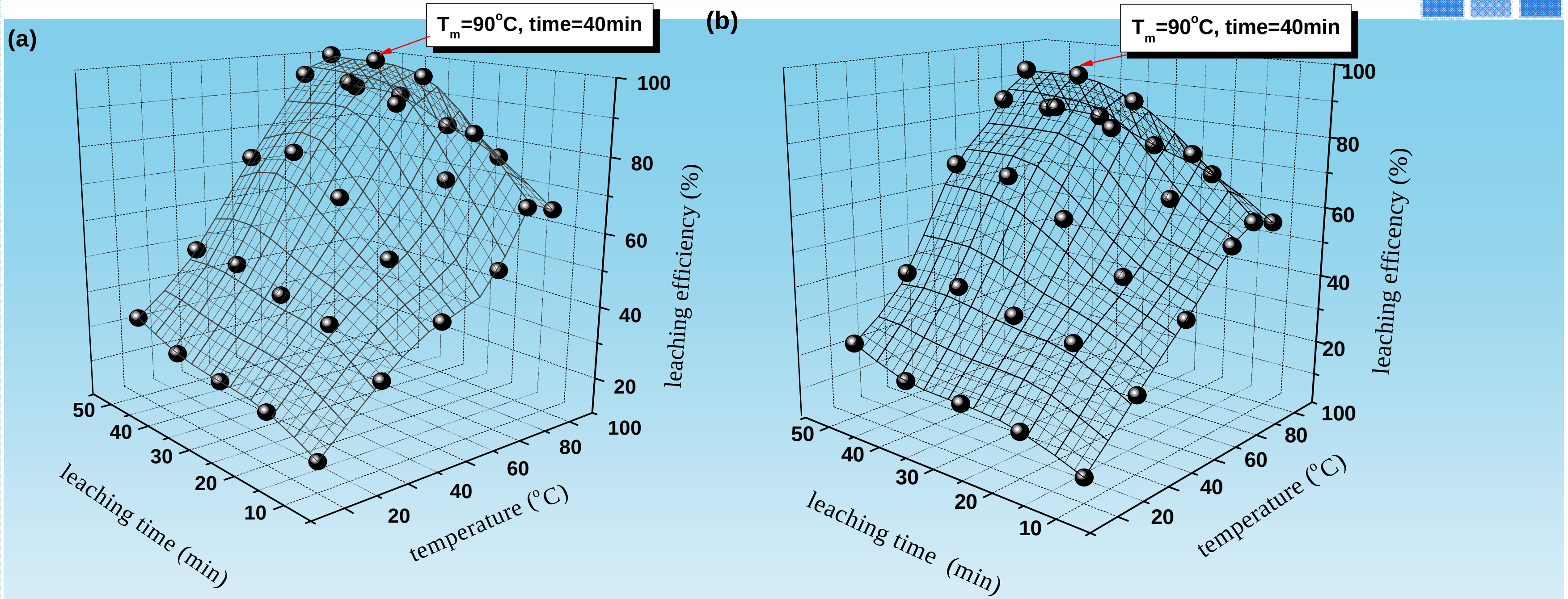


Fig. 6. Effect of leaching temperature and leaching time on the leaching of waste LiCoO2 with 1. 5 M malic acid (H2O2=2.0 vol.%., S:L= 20 gL−1 and agitation speed=300 rpm) leaching efficiency of Li and (b) leaching efficiency of Co.

- **Conditions for achieving a recovery of more than 90 wt.% Co and nearly 100 wt.% Li were determined experimentally by varying the concentrations of leachant, time and temperature of the reaction as well as the initial solid-to-liquid ratio.**
- **We found that hydrogen peroxide in a DL-malic acid solution is an effective reducing agent because it enhances the leaching efficiency. Leaching with 1.5 M DL-malic acid, 2.0 vol.% hydrogen peroxide and a S:L of 20 g L1 in a batch extractor results in a highly efficient recovery of the metals within 40 min at 90 C.**

Li Li, Feng Wu et al， Waste Management, 2010，30： 2615-2621

（3）Leaching process for $LiCoO_2$ materials using aspartic acids as leachant

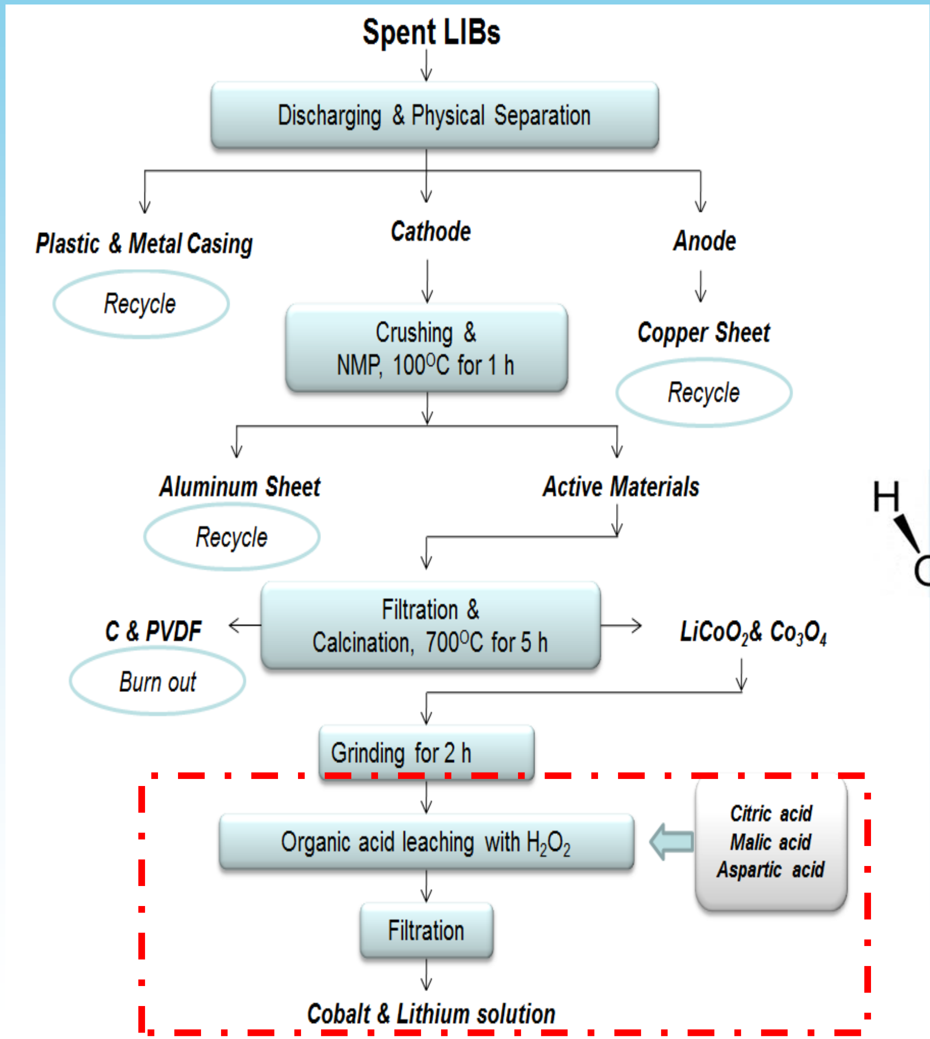
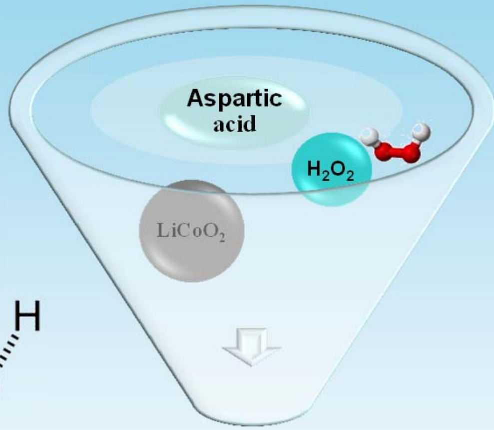
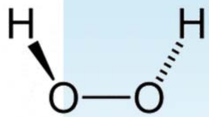
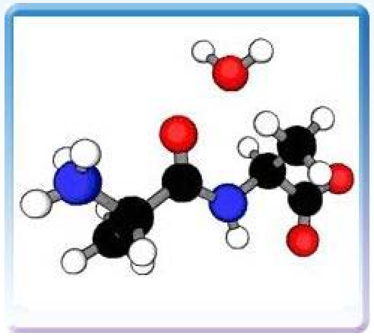


Fig.1. Flow sheet of the hydrometallurgical recycling process for spent LIBs.







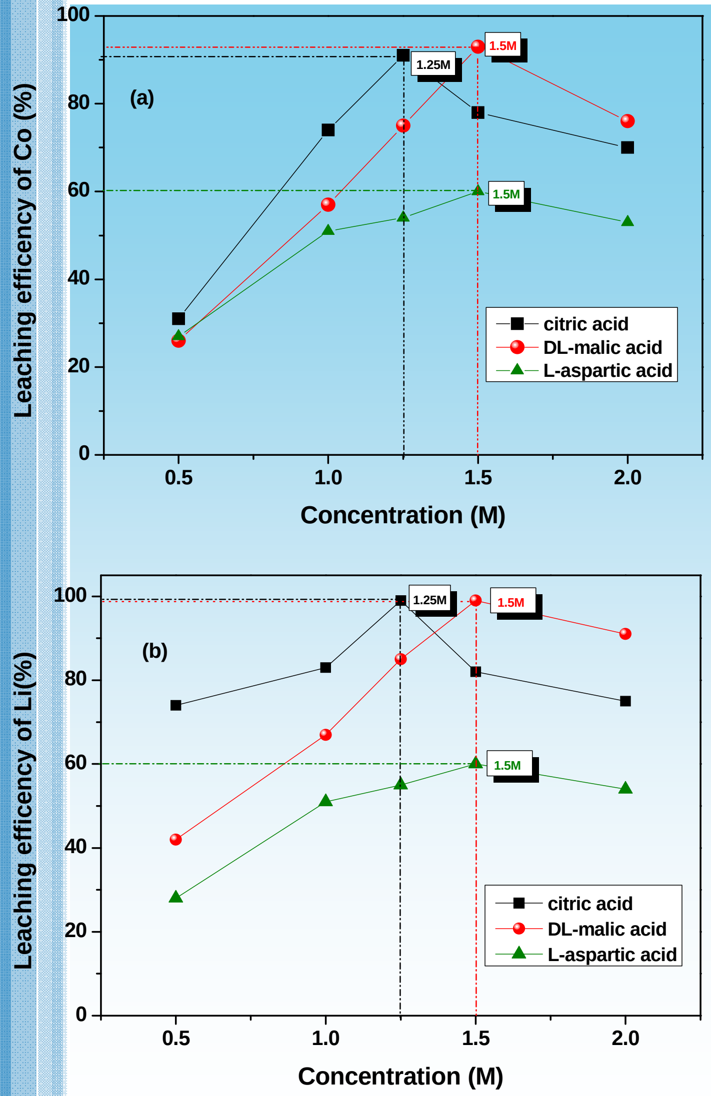


Fig. 5. Effect of acid concentration on the leaching of waste $LiCoO_2$

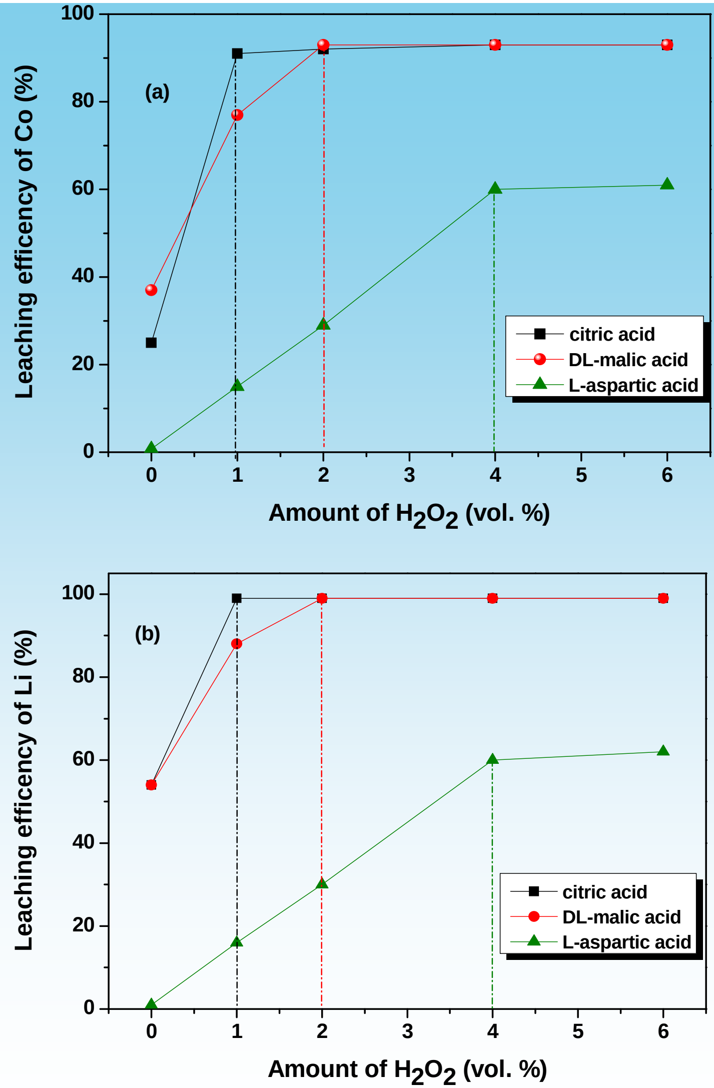


Fig. 6. Effect of H_2O_2 amount on the leaching of waste $LiCoO_2$

Li.Li, J.B.Dunn , L.Gaines, Feng Wu , K. Amine. Journal of Power Sources. 2013, 233：180-189

（4）Leaching process for $LiCoO_2$ materials using ascorbic acids as leachant

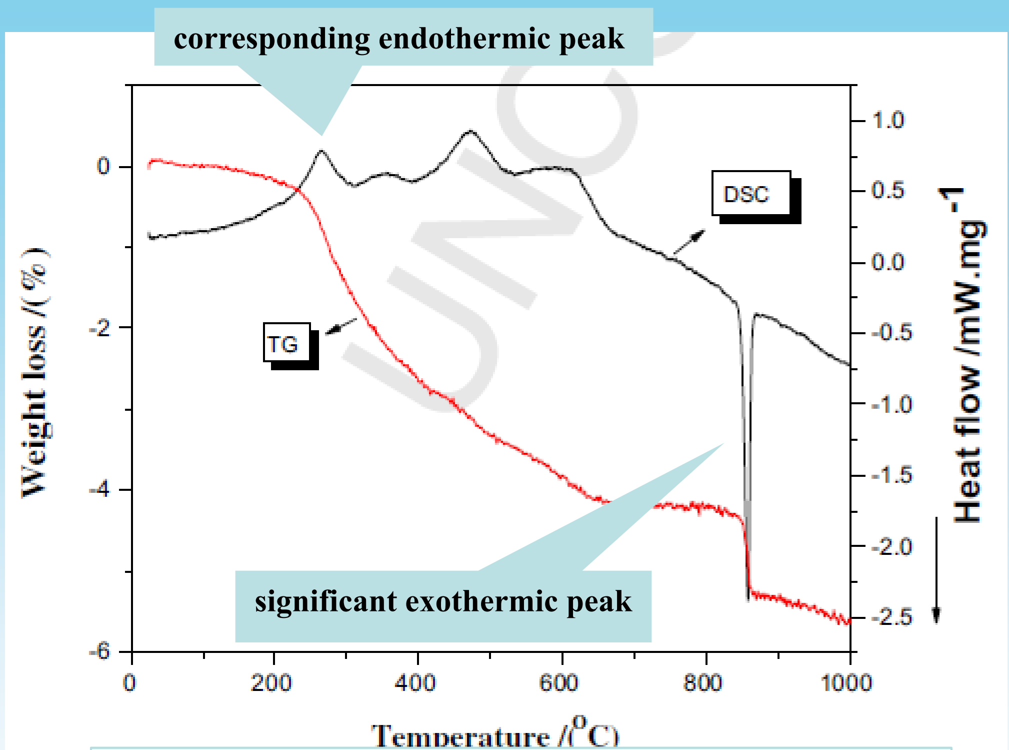


Fig. 2. TGA/DSC curves for the spent cathode materials

Table 1
TGA data for cathode materials.

	20–275 °C	275–700 °C	700–1000 °C
Weight loss (wt%)	0.98	3.2	1.45
Assignment	Loss of bound water	Burning of acetylene black and decomposition of PVDF	Phase change of $LiCoO_2$ and the loss of lithium

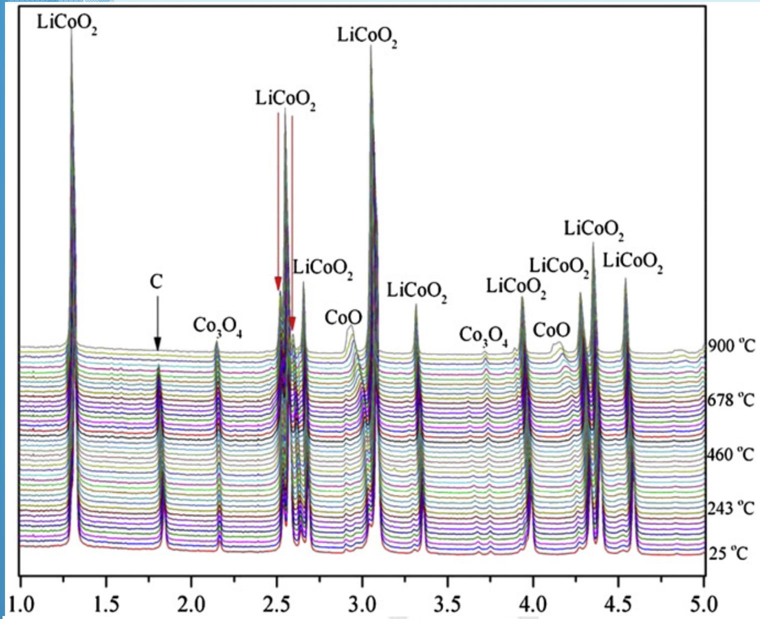


Fig. 3. In-situ XRD patterns of the samples during heat treatment from room temperature to 900 C.

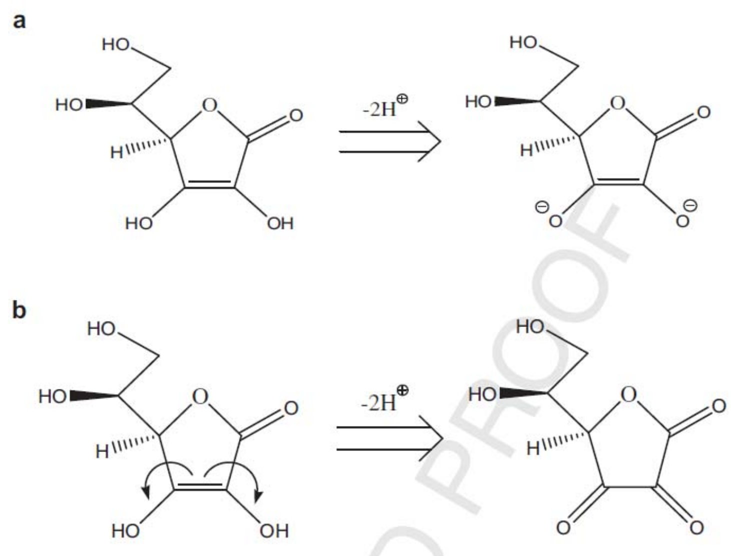
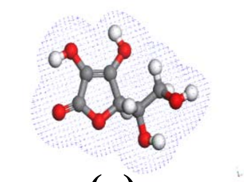
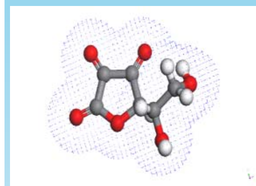


Fig. 6. The reaction of ascorbic acid as (a) organic acid and (b) reducing agent.



(a)



(b)

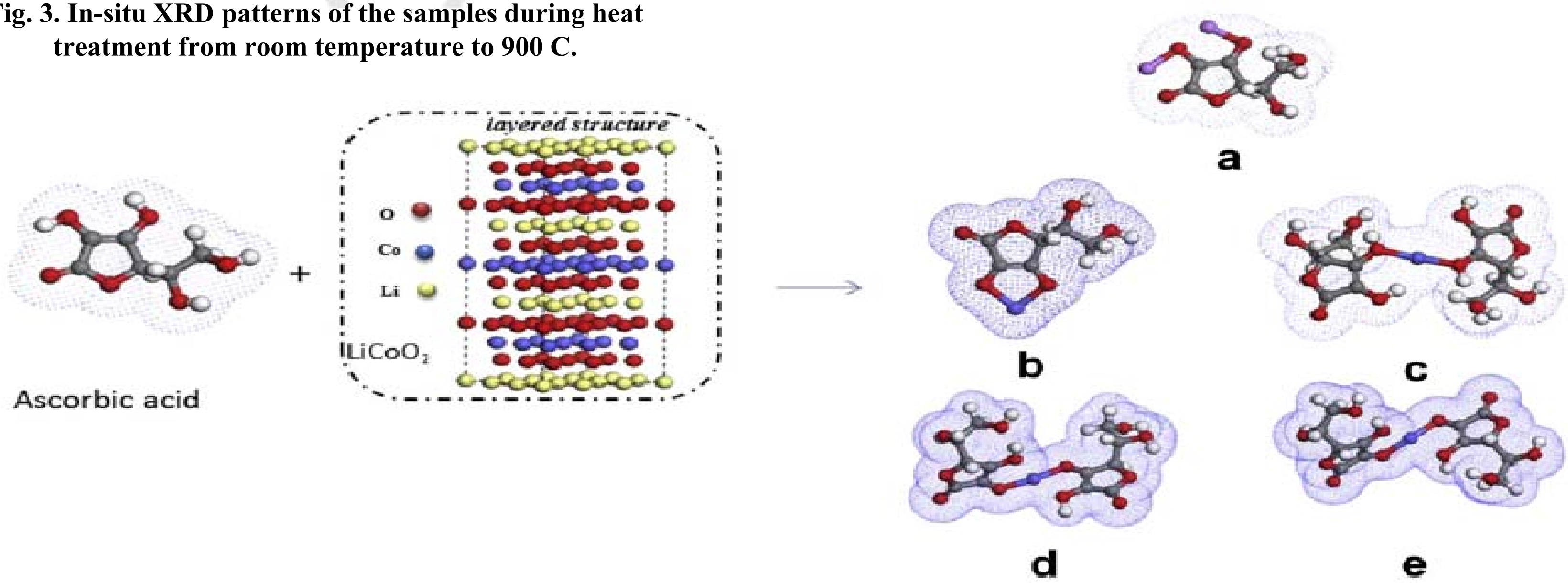
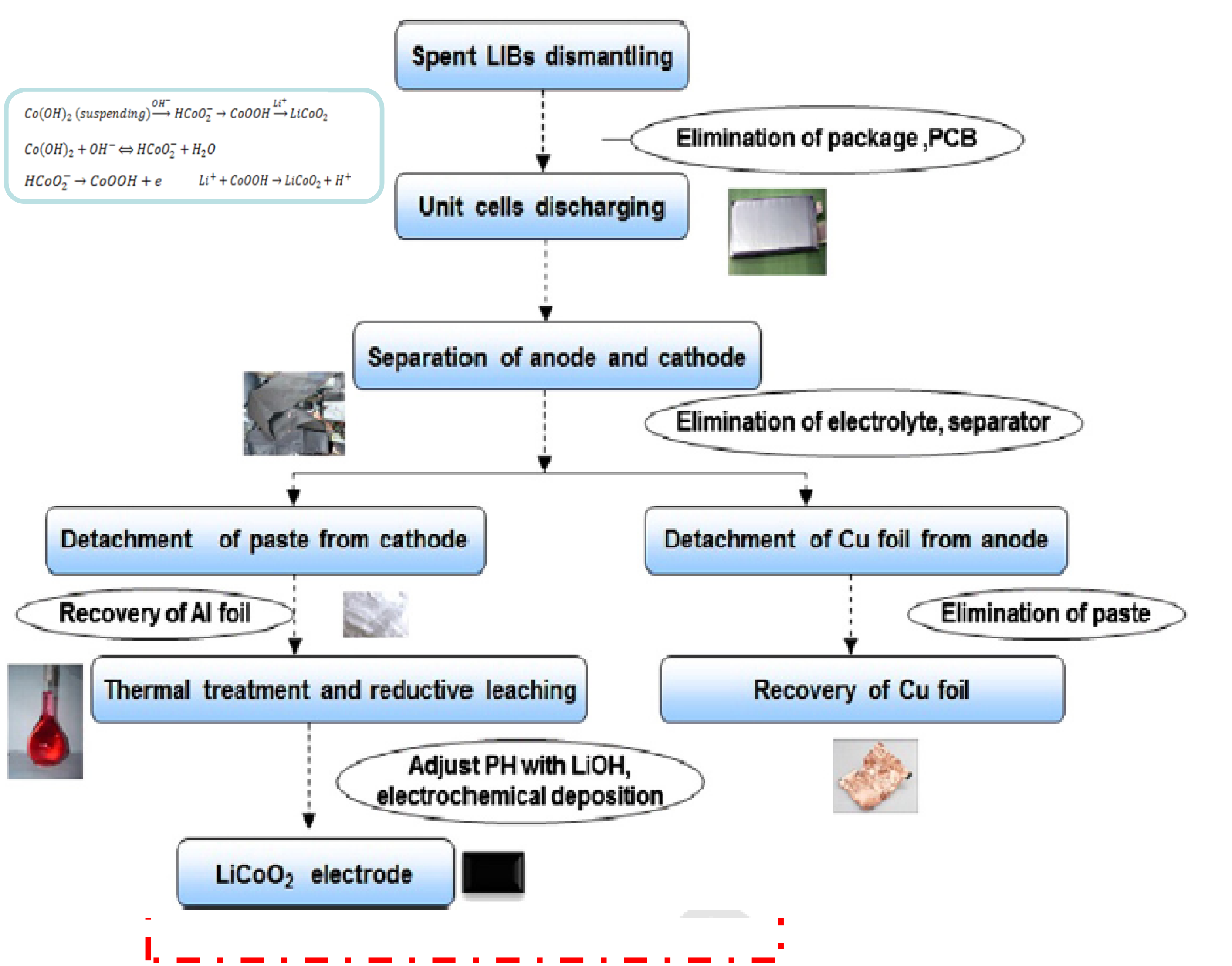


Fig. 7. Possible products of the leaching reaction of waste $LiCoO_2$ with ascorbic acid.

Li.Li, Jun Lu, Feng Wu , K. Amine. Journal of Power Sources.2012, Volume 218, 15. Pages 21–27

（5）Electrochemical deposition of $LiCoO_2$ materials from leaching Solutions



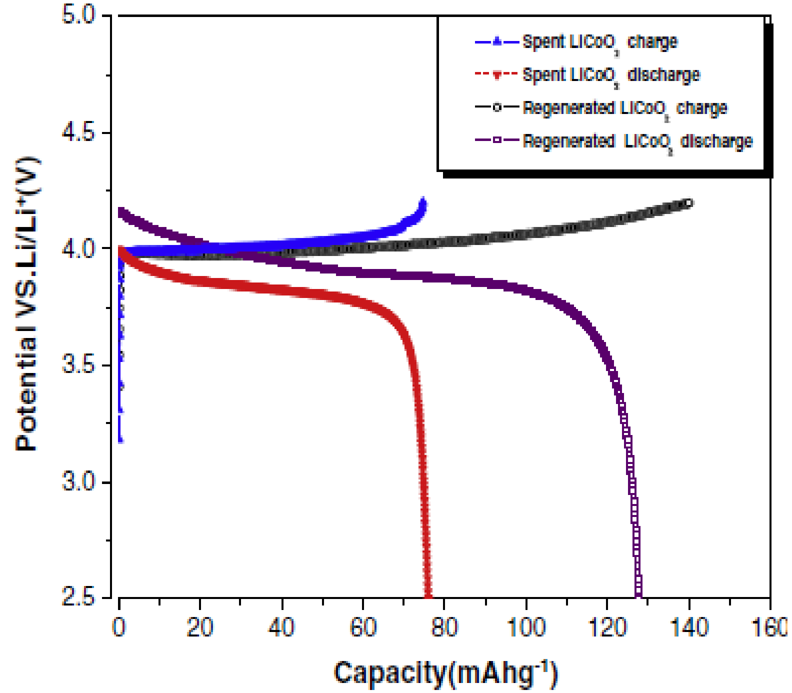


Fig. 7. Charge–discharge characteristics of the waste and regenerated $LiCoO_2$ at rate.

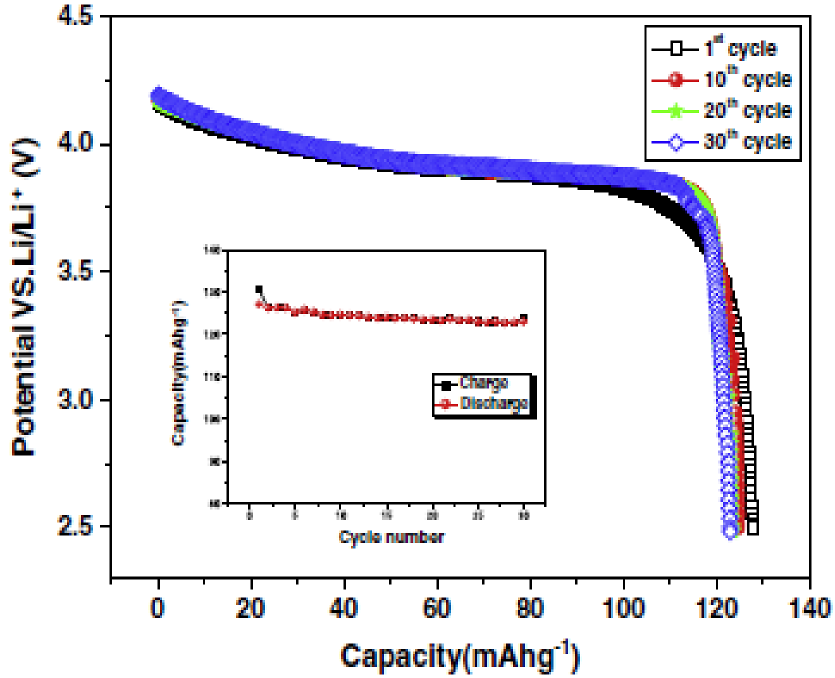


Fig. 9. Cycling performance of regenerated $LiCoO_2$ at 0.1 C rate.

- The charge potential plateau is reduced, and the discharge potential plateau is elevated by comparison with the used materials. The initial charge and discharge capacities were 130.8 and 127.1 mAh g−1, respectively.
- The discharge capacity of the LiCoO2 electrode was 122.9 mAh g−1 after 30 cycles, and the charge efficiency was 99.1%.
- Thus the regenerated LiCoO2 has good characteristics as a cathode active material in terms of cycling performance.

Li Li , Feng Wu et al，Hydrometallurgy, 108 (2011), pp. 220-225

Typical battery recycling companies in China-1

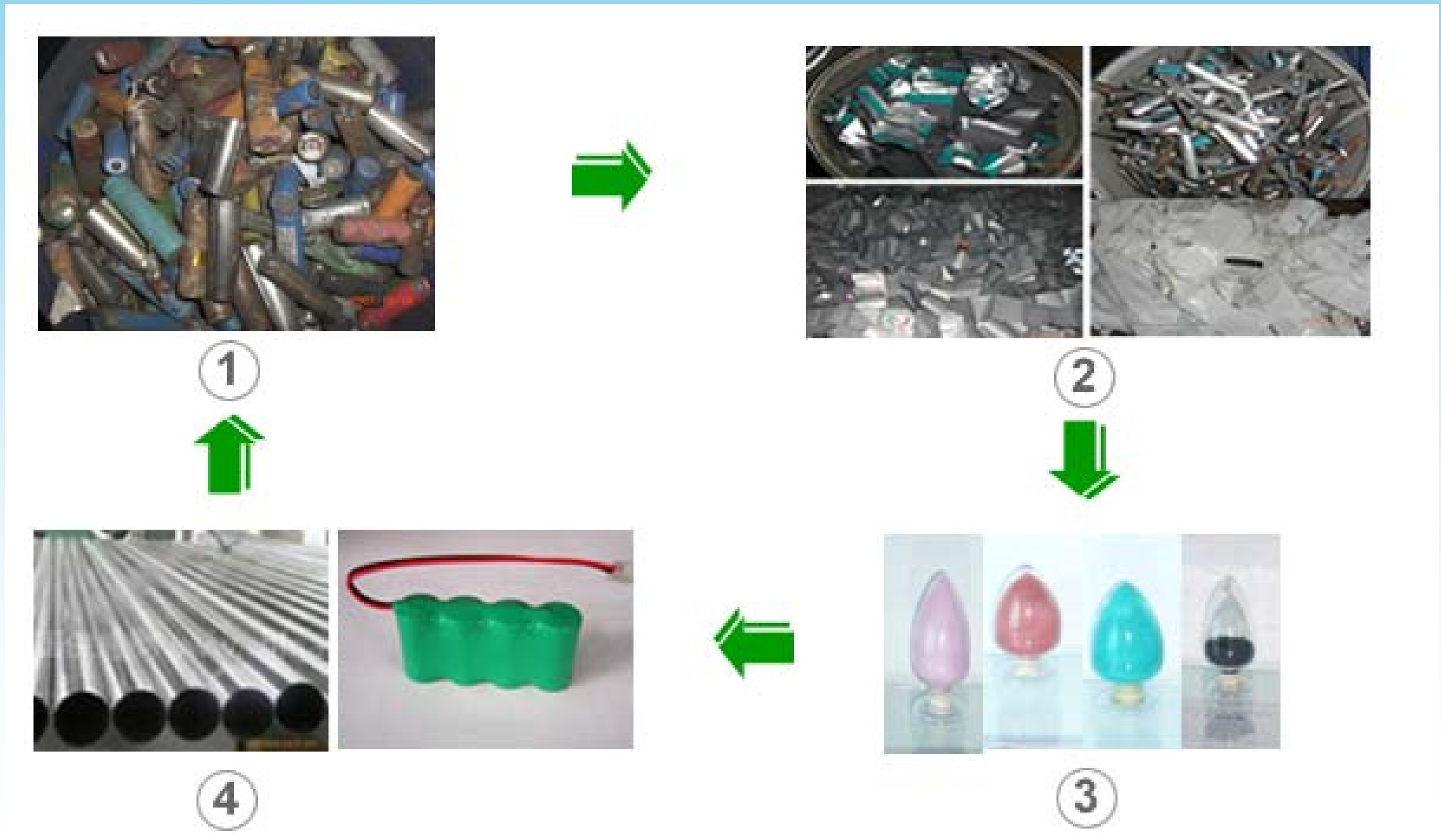
Shenzhen Green Eco-manufacture Hi-tech Co., Ltd

The flowchart of recycling process for spent batteries

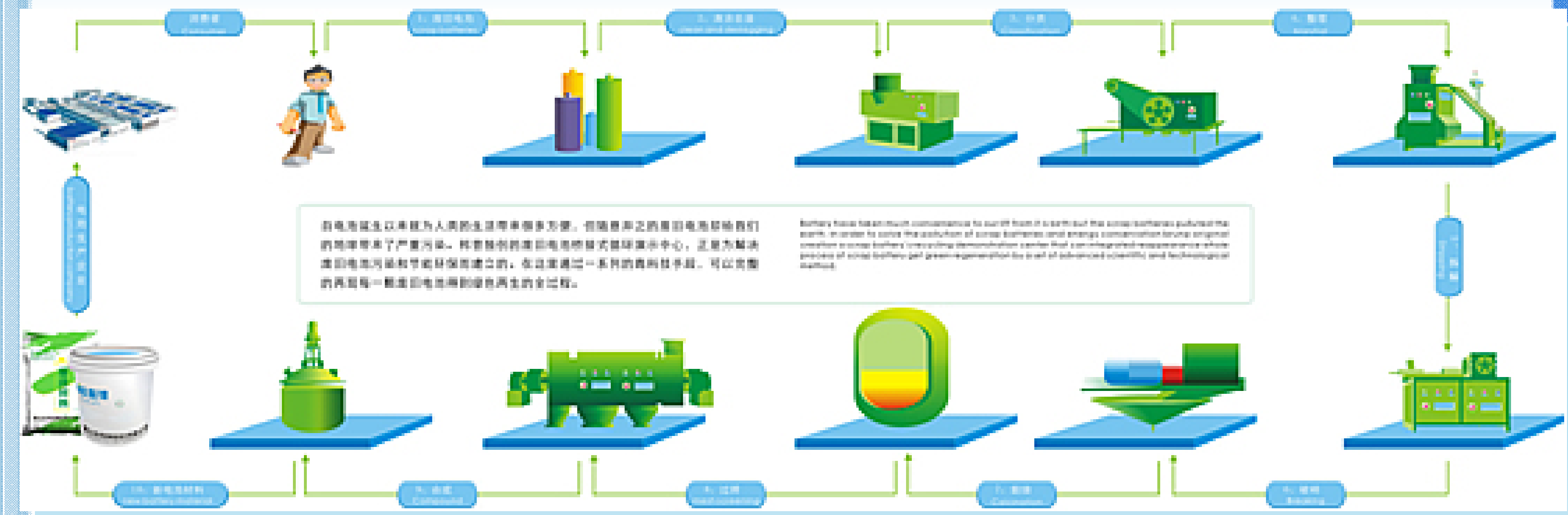
The flowchart of recycling process for spent batteries

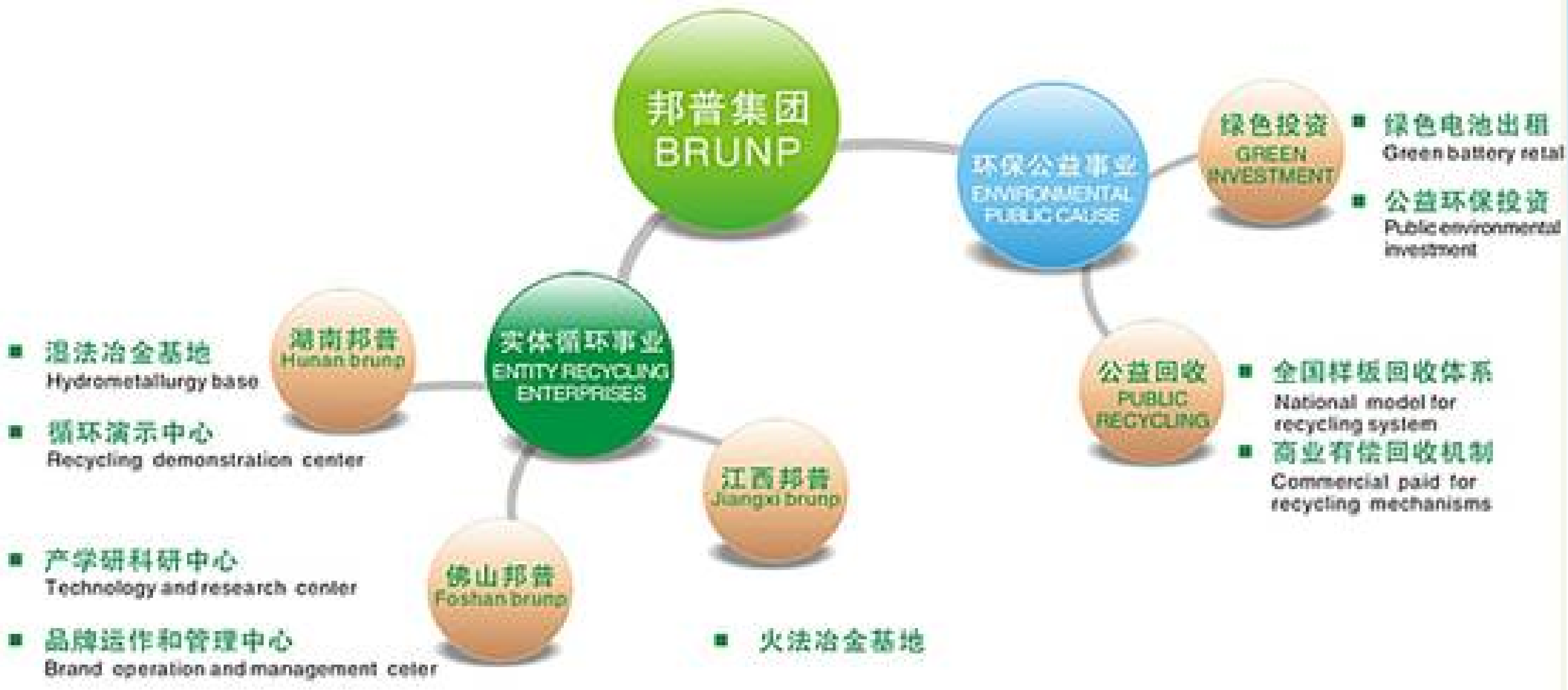
Typical battery recycling companies in China-2

FUOSHAN BANGPU NI/CO HIGH-TECH CO.,LTD



Demonstration center of recycling process for spent batteries

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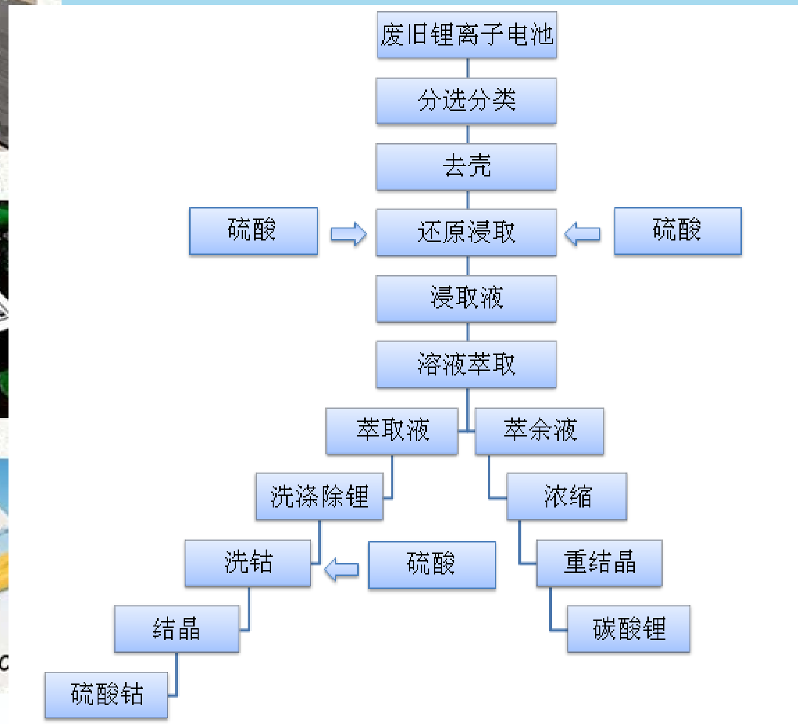
BRUNP
环保公益事业
ENVIRONMENTAL PUBLIC CAUSE
绿色投资
GREEN INVESTMENT
绿色电池出租
Green battery retal
公益环保投资
Public environmental investment
公益回收
PUBLIC RECYCLING
全国样板回收体系
National model for recycling system
商业有偿回收机制
Commercial paid for recycling mechanisms
实体循环事业
ENTITY RECYCLING ENTERPRISES
湖南邦普
Hunan brunp
湿法冶金基地
Hydrometallurgy base
循环演示中心
Recycling demonstration center
江西邦普
Jiangxi brunp
火法冶金基地
佛山邦普
Foshan brunp
产学研科研中心
Technology and research center
品牌运作和管理中心
Brand operation and management celer

Typical battery recycling companies in China-3

SHENZHEN TELE WASTE BATTERY RECYCLE. CO.,LTD




tele recycle
废旧电池回收

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Thanks for your attention！

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